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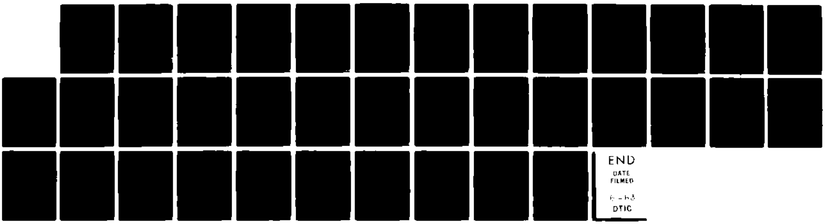

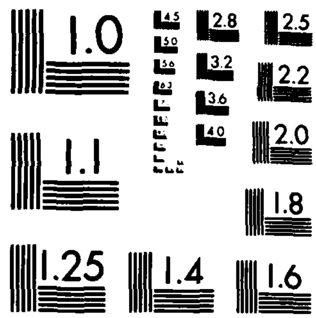
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Theory of Collision-Induced Ionization of Adsorbed Species on Solid Surfaces in the Presence of Laser Radiation

by

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A formalism is proposed for treating the problem of ionization of adsorbed species on solid surfaces. The ionizing agents are taken to be impact atoms and laser radiation with frequency low compared to the inverse of characteristic collision times. The physical constraints of short collision times and low laser frequency then allow one to treat the adatom-surface-plus-field system under the quasi-static approximation (QSA) and the impact-atom-adatom-surface collision dynamics under the impulse approximation (IMA). The latter leads to a time-dependent ionization cross-section which is factorizable into the square of an electron-atom scattering matrix element and

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a spectral function describing the energy-momentum distribution of electrons in the adatom-surface-plus-field system. The formalism focuses on the spectral function which is shown to be derivable from a single-particle Green's function exactly calculable for the present problem.

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Theory of Collision-Induced Ionization of Adsorbed Species on Solid Surfaces in the Presence of Laser Radiation

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Abstract

A formalism is proposed for treating the problem of ionization of adsorbed species on solid surfaces. The ionizing agents are taken to be impact atoms and laser radiation with frequency low compared to the inverse of characteristic collision times. The physical constraints of short collision times and low laser frequency then allow one to treat the adatom-surface-plus-field system under the quasi-static approximation (QSA) and the impact-atom-adatom-surface collision dynamics under the impulse approximation (IMA). The latter leads to a time-dependent ionization cross-section which is factorizable into the square of an electron-atom scattering matrix element and a spectral function describing the energy-momentum distribution of electrons in the adatom-surface-plus-field system. The formalism focuses on the spectral function which is shown to be derivable from a single-particle Green's function exactly calculable for the present problem.

I. Introduction

Photoemission studies of adsorbed species on solid surfaces, both theoretical[1-3] and experimental,[4-6] have produced considerable information on the nature of chemical bonding between adsorbed atoms or molecules and solid surfaces. The process of collision-induced ionization of surfaces, of potential importance in generating the same information, has, however, claimed relatively little attention, due to the widespread belief that it would be extremely difficult to extract useful experimental information from such studies. In this area, new ground has been broken recently by Conrad et al.,[7] who considered theoretically the problem of surface Penning ionization of a single CO molecule chemisorbed on a Pd(111) surface by metastable He*-beams and compared their results with existing experimental data. On another front, gas-phase studies of Penning ionization also suggest that laser radiation can have pronounced effects on the emitted-electron energy spectrum[8,9] as well as the ionization probability itself.[10] These works all point to the likely fruitfulness of carrying out studies on collision-induced ionization of adsorbed species on solid surfaces in the presence of laser radiation. In this paper, we will propose a formalism to treat this problem.

The physical situation we are considering may entail several competing processes in addition to the emission of electrons. There may be desorption[11] and migration[12] of adatoms, or even formation of free ions. However, the degree of catastrophe induced on the surface by the atom beam and the laser radiation is not entirely

beyond the experimentalist's control. Laser power and laser frequency, for instance, could be selected to minimize desorption and migration, and the incident-atom impact energy could conceivably be adjusted such that free-ion formation does not compete significantly with pure scattering. Also the amount of internal excitation carried by the impact-atoms may be tailored to preferentially ionize the adsorbed atoms rather than those of the bulk medium.

The main advantage of the laser as an inducing tool in the present case is that it has much greater versatility here than, say, in the process of laser-induced desorption, because no resonance requirement on the laser frequency need be imposed. We will, however, assume that the laser frequency is much less than characteristic band structure resonances of the pure metallic surface so that photoemission need not be considered as a competing process. We also require it not to be in resonance with adatom vibration or phonon coupling modes so as to avoid dealing with desorption or migration of adsorbed species.

Since the laser frequency is considered to be low, most of the energy required for ionization will have to be supplied by the internal excitation energy and the translational kinetic energy of the incident atoms. Hence we consider projectile atoms in an excited state with large impact velocities, leading to short collision times τ such that $\tau << \omega_L^{-1}$, where ω_L is the laser frequency. This means that the laser photons will only have a relatively short time in delivering energy. But since the adsorbed atom (adatom) states can

be considered to be broadened by the solid surface into a "near-continuum of states"[13] (with large uncertainties in orbital energies), the low frequency photons may still be effective in transferring energy to electronic degrees of freedom in the adatom-surface system, facilitating electron "hops" between the adatom and the surface.[14] This would not be the case if sharp resonance electronic states were considered (such as in gas-phase collisions).

The conditions of short collision time and low laser frequency permits the use of the quasi-static approximation (QSA) where, even though the total Hamiltonian is time-dependent (due to the radiation interaction), the energy of the system is considered to be adiabatically conserved within the duration of a characteristic collision time [cf. Eqs.(2.6) and (2.7) below]. Also, the smallness of τ warrants the use of the impulse approximation[15] (IMA) in the treatment of the projectile atom-adatom-surface collision dynamics. Within this approximation, the collision between the projectile atom and the adatom-surface (AS) system is assumed to be mediated by a single electron possessing a characteristic momentum and energy distribution determined by virtue of its being part of the adatom-surface plus field system and otherwise considered to be free. Naturally the IMA will be more suitable when applied to cases where the adatom-surface system to be ionized has loosely bound electrons. The momentum and energy distribution will be most conveniently obtained through a Green's function formalism. The IMA has been successfully applied to a wide variety of collision processes, such as fast electron-atom collisions,[16] A(p,2p)B scattering in nuclear reactions,[17,18] and gas-phase collisional ionization.[19] Recently, we have also applied it to high-energy positron ionization of adsorbed species,[20] a process closely related to that discussed in the present work.

In what follows we will construct a formalism for the calculation of the differential cross section of the ionization process. This formalism is based largely on many-body techniques leading to the construction of an adatom-surface-plus-field Green's function that is time-dependent. The implementation of the main approximations, the QSA and the IMA, will be shown in the course of the development.

II. The Ionization Cross-Section

We consider the process in which projectile atoms B with momentum $\vec{p}_i$ are incident on an adatom-surface (AS) system which is driven by monochromatic laser radiation with field strength represented classically by $\vec{E}(t) = \vec{E}_0 \cos\omega_L t$, where ω_L is the laser frequency. Assuming that this collisional process leads to ionization with emitted electron momentum and final momentum for the atoms B equal to $\vec{p}$ and $\vec{p}_f$ respectively, the time-dependent differential ionization cross-section can in general be written in the form[17]

$$d^6\sigma(t) = \frac{2\pi}{\hbar}\sum_{(+)}|T(t)|^2\delta\{\varepsilon+\varepsilon_f+E^{(+)}(t)-(E_0(t)+\varepsilon_i+\Delta)\}\frac{1}{v_0}\,\frac{d^3p\,d^3p_f}{(2\pi h)^3}\;. \quad (2.1)$$

In Eq.(2.1) v_0 is the incident velocity of B atoms;

$$\varepsilon = p^2/2m, \quad (2.2)$$

$$\varepsilon_i = p_i^2/2m_B, \quad (2.3)$$

and

$$\varepsilon_f = p_f^2/2m_B \quad (2.4)$$

are the kinetic energies of the emitted electron and the free atoms B before and after the collision respectively, with m = mass of

electron and m_B = mass of atom B; and

$$\Delta = E_i - E_f, \tag{2.5}$$

the internal energy transfer, is the *difference* between the initial and final internal energies of the atom B. The presence of the δ-function with time-dependent energy variables follows from the quasi-static approximation (QSA), where it is assumed that if the collision time τ is short enough compared with the period of the driving force, the ground state energy E_0 and excited energies $E^{(+)}$ of the unperturbed and singly-ionized AS+field system vary adiabatically over $t < \tau$; also, the total energy of the system is adiabatically conserved. The QSA then implies that

$$\hat{H}_{AS}(t)|\Psi_0(t)\rangle \simeq E_0(t)|\Psi_0(t)\rangle, \tag{2.6}$$

and

$$\hat{H}_{AS}(t)|\Psi^{(+)}(t)\rangle \simeq E^{(+)}(t)|\Psi^{(+)}(t)\rangle, \tag{2.7}$$

where $\hat{H}_{AS}(t)$ is the total time-dependent Hamiltonian of the AS system plus field; and $|\Psi_0(t)\rangle$ and $|\Psi^{(+)}(t)\rangle$ are the corresponding adiabatic ground state and excited state wave functions, unperturbed and singly-ionized, respectively. The summation in Eq.(2.1) is over all the final singly-ionized AS states $|\Psi^{(+)}(0)\rangle$, where it is assumed that at t=0, the laser field is turned on. Within the impulse approximation (IMA), the transition matrix element T can be written as

$$T(t) = \langle\Psi^{(+)}(t)|\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle T_{E_f,\vec{p}_f,\vec{p};E_i,\vec{p}_i,\vec{p}_1}, \tag{2.8}$$

where $\hat{a}(\vec{p}_1)$ is a fermion annihilation field operator (removing an electron of momentum $\vec{p}_1$ from the AS system in its ground state at time t) and $T_{E_f,\vec{p}_f,\vec{p};E_i,\vec{p}_i,\vec{p}_1}$ is an off-shell electron-atom scattering

matrix element, describing the collision between an atom B in the initial state $|i\rangle$ with kinetic energy $p_i^2/2m_B$ and a free electron with momentum $\vec{p}_1$, to produce an atom B in the state $|f\rangle$ with kinetic energy $p_f^2/2m_B$ and a free electron with momentum p. The IMA to T is schematically represented in Fig 1, in which ε_1 and $\vec{p}_1$ represent the energy and momentum removed from the AS+field system at time t. The IMA also implies that at the right vertex (blank circle) energy and momentum are both strictly conserved. Hence we have

$$\varepsilon_1 + \frac{p_i^2}{2m_B} + \Delta = \frac{p_f^2}{2m_B} + \frac{p^2}{2m} , \tag{2.9}$$

and

$$\vec{p}_1 + \vec{p}_i = \vec{p} + \vec{p}_f . \tag{2.10}$$

We first discuss the sum in Eq.(2.1). This equation, together with Eqs.(2.8) and (2.9), implies that the sum can be written as:

$$\begin{aligned} S(\vec{p}_1,\varepsilon_1,t) &\equiv \sum_{(+)} |\langle\Psi^{(+)}(t)|\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle|^2 \delta(\varepsilon_1+E^{(+)}(t)-E_0(t)) \\ &= \sum_{(+)} \langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)\delta(\varepsilon_1+E^{(+)}(t)-E_0(t))|\Psi^{(+)}(t)\rangle \\ &\qquad \times \langle\Psi^{(+)}(t)|\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle \\ &\approx \sum_{(+)} \langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)\delta(\varepsilon_1+H_{AS}(t)-E_0(t))\hat{U}_s^{(+)}(t,0)|\Psi^{(+)}(0)\rangle \\ &\qquad \times \langle\Psi^{(+)}(0)|\hat{U}_s^{(+)\dagger}(t,0)\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle \\ &= \langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)\delta(\varepsilon_1+H_{AS}(t)-E_0(t))\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle , \end{aligned} \tag{2.11}$$

where in the second equality use has been made of Eq.(2.7) (the QSA), and the time evolution operator, $\hat{U}_s^{(+)}(t,0)$, for the Schrödinger picture wave function $\Psi^{(+)}(t)$ has been introduced such that

$$\hat{U}_S^{(+)}(t,0)|\Psi_0^{(+)}(0)\rangle = |\Psi_0^{(+)}(t)\rangle . \qquad (2.12)$$

The quantity $S(\vec{p}_1,\varepsilon_1,t)$ is referred to as the time-dependent spectral function and can be interpreted as the probability at time t of finding an electron with momentum $\vec{p}_1$ in the AS+field system and the energy $E_0(t)-\varepsilon_1$ in the residual system after an electron has been removed. The differential ionization cross-section can then be written as:

$$d^6\sigma(t) = \frac{2\pi}{\hbar} S(\vec{p}_1,\varepsilon_1,t)|T_{E_f,\vec{p}_f,\vec{p};E_i,\vec{p}_i,\vec{p}_1}|^2 \frac{1}{v_0} \frac{d^3p\,d[illegible]}{(2[illegible]} . \qquad (2.13)$$

The time-dependent spectral function can be shown [illegible] be related to the Fourier Transform of the advanced single-partic[illegible] Green's function as follows. We start with the definition of the advanced single-particle Green's function;

$$G_A(\vec{p}_1;t,t') \equiv i\langle\Psi_0|\hat{a}_H^\dagger(\vec{p}_1,t)\hat{a}_H(\vec{p}_1,t')|\Psi_0\rangle\theta(t-t') \qquad (2.14)$$

where

$$|\Psi_0\rangle \equiv |\Psi_0(0)\rangle , \qquad (2.15)$$

and $\theta(t-t')$ is the Heaviside step function. $\hat{a}_H(\vec{p}_1,t)$ is the time-dependent Heisenberg picture fermion annihilation field operator given as:

$$\hat{a}_H(\vec{p}_1,t) = \hat{U}_S^\dagger(t,0)\hat{a}(\vec{p}_1)\hat{U}_S(t,0) , \qquad (2.16)$$

with $\hat{U}_S(t,0)$ satisfying the relation

$$|\Psi_0(t)\rangle = \hat{U}_S(t,0)|\Psi_0\rangle . \qquad (2.17)$$

We can then write the advanced Green's function as

$$G_A(\vec{p}_1;t,t') = i\langle\Psi_0|\hat{U}_S^\dagger(t,0)\hat{a}^\dagger(\vec{p}_1)\hat{U}_S(t,0)\hat{U}_S^\dagger(t',0)\hat{a}(\vec{p}_1)\hat{U}_S(t',0)|\Psi_0\rangle\theta(t-t')$$
$$= i\langle\Psi_0|\hat{U}_S^\dagger(t,0)\hat{a}^\dagger(\vec{p}_1)\hat{U}_S(t,t')\hat{a}(\vec{p}_1)\hat{U}_S(t+t_1,t)\hat{U}_S(t,0)|\Psi_0\rangle\theta(-t_1)$$
$$= i\langle\Psi_0|\hat{U}_S^\dagger(t,0)\hat{a}^\dagger(\vec{p}_1)\hat{U}_S^\dagger(t+t_1,t)\hat{a}(\vec{p}_1)\hat{U}_S(t+t_1,t)\hat{U}_S(t,0)|\Psi_0\rangle\theta(-t_1)$$
$$= i\langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)\hat{U}_S^\dagger(t+t_1,t)\hat{a}(\vec{p}_1)\hat{U}_S(t+t_1,t)|\Psi_0(t)\rangle\theta(-t_1). \tag{2.18}$$

In the second equality above we have made the change of time variables

$$t_1 = t' - t \tag{2.19}$$

and use of the property for the time evolution operator $\hat{U}_S$ that

$$\hat{U}_S(t_1,t_2)\hat{U}_S(t_2,t_3) = \hat{U}_S(t_1,t_3). \tag{2.20}$$

Under the QSA we can write

$$\hat{U}_S(t_1+t,t) \simeq \exp\{-\frac{i}{\hbar}\hat{H}_{AS}(t)t_1\} \tag{2.21}$$

if $|t_1| \lesssim \tau$ and it follows that

$$G_A(\vec{p}_1;t,t+t_1) \simeq i\langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)e^{\frac{i}{\hbar}(\hat{H}_{AS}(t)-E_0(t))t_1}\theta(-t_1)\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle,$$
$$|t_1| \lesssim \tau. \tag{2.22}$$

Introducing the integral representation for the step function

$$\theta(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty}d\omega\,\frac{e^{-i\omega t}}{\omega+i\eta} \tag{2.23}$$

we have

$$\theta(-t_1)\exp\{\frac{i}{\hbar}(\hat{H}_{AS}(t)-E_0(t))t_1\} = \frac{1}{2\pi i}\int_{-\infty}^{\infty}d\omega\frac{e^{-i\omega t_1}}{\omega+\frac{1}{\hbar}[\hat{H}_{AS}(t)-E_0(t)]-i\eta}. \tag{2.24}$$

Hence the restricted Fourier Transform of $G_A(\vec{p}_1;t,t_1+t)$ can be written

as

$$\tilde{G}_A(\vec{p}_1,\omega,t) = \langle\Psi_0(t)|\hat{a}^\dagger(\vec{p}_1)\frac{1}{\omega+\frac{1}{\hbar}[\hat{H}_{AS}(t)-E_0(t)]}\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle. \qquad (2.25)$$

From Eq.(2.11), the relation between the spectral function and the restricted advanced Green's function is then

$$S(\vec{p}_1,\varepsilon_1,t) = \frac{1}{2\pi i\hbar}\lim_{\eta\to 0}[\tilde{G}_A(\vec{p}_1,\omega_1-i\eta,t) - \tilde{G}_A(\vec{p}_1,\omega_1+i\eta,t)]$$

$$= \frac{1}{\pi\hbar}\lim_{\eta\to 0} \mathrm{Im}\, \tilde{G}_A(\vec{p}_1,\omega_1-i\eta,t), \qquad (2.26)$$

where

$$\hbar\omega_1 \equiv \varepsilon_1 \qquad (2.27)$$

and the representation for the delta function

$$\delta(x) = \frac{1}{2\pi i}\lim_{\eta\to 0}\left(\frac{1}{x-i\eta} - \frac{1}{x+i\eta}\right) \qquad (2.28)$$

has been used. We note that in arriving at Eq.(2.25) the restricted Fourier Transform is taken as though $\hat{U}_S(t_1+t,t)$ assumes for all t_1 the functional form dictated by $|t_1| \lesssim \tau$, that is, the Hamiltonian entering into the computation of $G_A(\vec{p}_1;t,t')$ is just $\hat{H}_{AS}(t)$ [cf. Eq.(2.21)]. The restricted transform is, of course, distinct from the true transform

$$\hat{G}_A(\vec{p}_1,\omega,t) = \int_{-\infty}^{\infty} dt_1\, e^{i\omega t_1} G_A(\vec{p}_1;t,t'),\ t_1=t'-t. \qquad (2.29)$$

The computation of $G_A(\vec{p}_1,t,t')$ will be discussed in the next section, and that of $\hat{G}(\vec{p}_1,\omega,t)$ in Appendix I.

We now turn our attention to $T_{E_f,\vec{p}_f,\vec{p};\, E_i,\vec{p}_i,\vec{p}_1}$, the electron-atom scattering matrix element. This is a well-studied problem which we will not pursue in detail.[16] Under ordinary situations where only

$\vec{p} >> \vec{p}_f$ leads to significant cross-sections in Eq.(2.1), the Born approximation can usually be applied. In this case

$$T_{E_f,\vec{p}_f,\vec{p};E_i,\vec{p}_i,\vec{p}_1} = \int d^3r e^{i\vec{q}\cdot\vec{r}} \langle f|V(\vec{r}-\vec{x})|i\rangle \tag{2.30}$$

where $\hbar\vec{q}$, the electronic momentum transfer, is given by

$$\hbar\vec{q} \simeq \vec{p}_1 - (m/m_B)\vec{p}_i - [\vec{p} - (m/m_B)\vec{p}_f] \tag{2.31}$$

and $V(\vec{r}-\vec{x})$ is the electrostatic interaction between an electron (with coordinate $\vec{r}$) and the electrons in atom B (with collective coordinates $\vec{x}$).

III. Development of the Green's Function in the Presence of an External Field - Time-dependent Spectrum

We wish to calculate the space-time Green's function

$$G(\vec{x}',t';\vec{x},t) \equiv -i\langle\Psi_0|T[\hat{a}_H(\vec{x}',t')\hat{a}_H^\dagger(\vec{x},t)]|\Psi_0\rangle \tag{3.1}$$

(and its Fourier Transform) where T denotes the time-ordered product, $\hat{a}_H(\vec{x},t)$ is the time-dependent Heisenberg picture fermion creation field operator and $|\Psi_0\rangle$ satisfies [cf. Eq.(2.15)]

$$\langle\Psi_0|\Psi_0\rangle = 1. \tag{3.2}$$

$\hat{a}_H(\vec{x},t)$ is the Fourier Transform of $\hat{a}_H(\vec{p},t)$ [cf. Eq.(2.14)]:

$$\hat{a}_H(\vec{x},t) = \frac{1}{(2\pi)^3\hbar^{3/2}}\int d^3p\, e^{\frac{i}{\hbar}\vec{p}\cdot\vec{x}}\hat{a}_H(\vec{p},t). \tag{3.3}$$

We assume that the separate problems of the adatom orbitals $\phi_i(\vec{x})$ and the self-consistent eigenstates $\phi_\sigma(\vec{x})$ of the unperturbed semi-infinite surface are solved so that the time-independent field operators can be expressed as

$$\hat{a}(\vec{x}) = \sum_i \hat{a}_i \phi_i(\vec{x}) + \sum_\sigma \hat{a}_\sigma \phi_\sigma(\vec{x}) = \hat{a}_H(\vec{x},0). \tag{3.4}$$

The surface is taken to be metallic and σ includes the wave number and the band index. $\hat{a}_i$ and $\hat{a}_\sigma$ are the electron annihilation operators for the i^{th} adatom state and σ^{th} surface state, respectively. Each electron in the adatom-surface plus field system is considered to be under the influence of a self-consistent field so that the single-particle Hamiltonian can be written as

$$h_{AS}(\vec{x},t) = h(\vec{x}) - e\vec{E}_0 \cdot \vec{x}\theta(t)\cos\omega_L t. \tag{3.5}$$

where the second term is the classical interaction Hamiltonian between an electron at $\vec{x}$ and an external laser field of field strength E_0 and frequency ω_L (in the dipole approximation). The field-free Hamiltonian $h(\vec{x})$ is assumed to have the properties

$$\langle\phi_i|h|\phi_j\rangle = \varepsilon_i\delta_{ij} \tag{3.6}$$

$$\langle\phi_\sigma|h|\phi_{\sigma'}\rangle = \varepsilon_\sigma\delta_{\sigma\sigma'} \tag{3.7}$$

where ε_i and ε_σ are energies belonging to the states ϕ_i and ϕ_σ with the adatom at infinite distance from the surface. The interaction leading to adsorption is given by the matrix elements

$$\langle\phi_i|h|\phi_\sigma\rangle \equiv V_{i\sigma}. \tag{3.8}$$

Using the basis $\{\phi_i,\phi_\sigma\}$, h can then be written in matrix form as

$$\underset{\sim}{h} = \left(\begin{array}{ccc:ccc} \varepsilon_i & & 0 & & & \\ & \ddots & & & v_{i\sigma} & \\ 0 & & \varepsilon_j & & & \\ \hdashline & & & \varepsilon_\sigma & & 0 \\ & v^*_{i\sigma} & & & \ddots & \\ & & & 0 & & \varepsilon_{\sigma'} \end{array}\right) \tag{3.9}$$

It is also convenient for the computation of the Green's function, to write the total single-particle Hamiltonian as

$$\begin{aligned} h_{AS}(\vec{x},t) &= h_0(\vec{x}) + h_1(\vec{x}) + h_f(\vec{x},t) \\ &\equiv h_0(\vec{x}) + h_I(\vec{x},t) \end{aligned} \tag{3.10}$$

where $h_f(\vec{x},t) \equiv -e\vec{E}_0\cdot\vec{x}\theta(t)\cos\omega_L t$ and $h_0(\vec{x})$ corresponds to only the diagonal elements in Eq.(3.9). The total Hamiltonian in second quantized form is then given by

$$\begin{aligned} \hat{H}_{AS}(t) &= \int d^3x\ \hat{a}^\dagger(\vec{x})h_{AS}(\vec{x},t)\hat{a}(\vec{x}) \\ &= \sum_\sigma \hat{a}_\sigma^\dagger\hat{a}_\sigma\varepsilon_\sigma + \sum_i \hat{a}_i^\dagger\ \hat{a}_i\varepsilon_i + \sum_{i\sigma}(V_{i\sigma}(t)\hat{a}_i^\dagger\ \hat{a}_\sigma + V^*_{i\sigma}(t)\hat{a}_\sigma^\dagger\ \hat{a}_i) \\ &\quad + \sum_{\sigma\neq\sigma'}\hat{a}_\sigma^\dagger\ \hat{a}_{\sigma'}u_{\sigma\sigma'}(t) + \sum_{i\neq i'}\hat{a}_i^\dagger\ \hat{a}_{i'}\ u_{ii'}(t) \end{aligned} \tag{3.11}$$

where

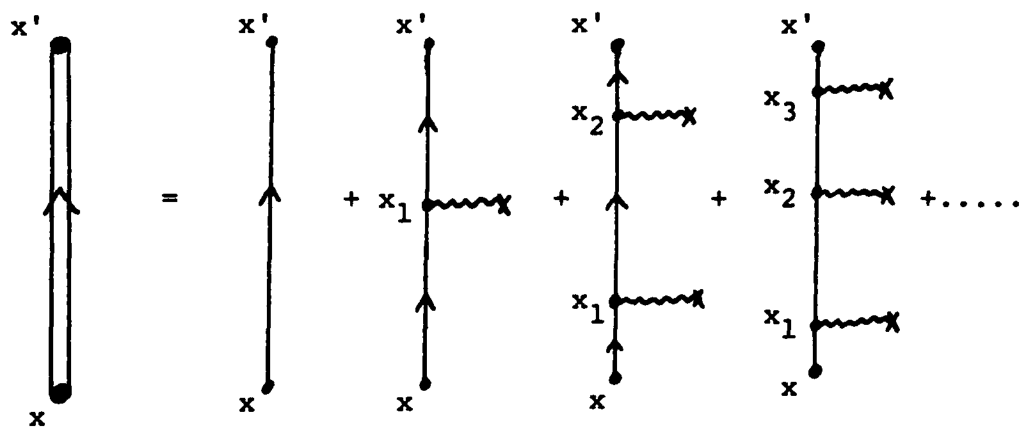
$$\begin{aligned} V_{i\sigma}(t) &= \langle\phi_i|h_I(\vec{x},t)|\phi_\sigma\rangle \\ &= v_{i\sigma} + u_{i\sigma}(t), \end{aligned} \tag{3.12}$$

and

$$u_{ab}(t) = \langle a|h_f(\vec{x},t)|b\rangle \tag{3.13}$$

with a,b standing for $\{i\}$ or $\{\sigma\}$. In Eq.(3.11) the first two terms describe "unperturbed" electrons corresponding to the states $|\phi_i\rangle$ and $|\phi_\sigma\rangle$; the third term accounts for the combined effects of adsorptive and radiative interaction between the states $|\phi_i\rangle$ and $|\phi_\sigma\rangle$; and the last two terms describe radiative interactions within the sets of states $|\phi_\sigma\rangle$ and $|\phi_i\rangle$ respectively.

Since the interaction Hamiltonian h_I only involves single-particle coordinates [cf. Eq.(3.10)], the series expansion of the Green's function [defined in Eq.(3.1)] assumes a particularly simple form. The usual expansion procedure using Wick's theorem[21] leads to the following diagrammatic representation for G(x',x):



(3.14)

where the contracted notation x stands for the space-time point $(\vec{x},t)$, etc.; the double bar and the single bar stand for the full

Green's function and the "non-interacting" Green's function respectively; and the wavy lines stand for the interactions h_I integrated over intermediate space-time variables. Eq.(3.14) is equivalent to

$$G(x'x) = G^0(x',x) + \frac{1}{\hbar}\int d^4x_1\; G^0(x',x_1)h_I(x_1)G_0(x_1,x)$$
$$+(\frac{1}{\hbar})^2\int d^4x_1 d^4x_2 G^0(x',x_2)h_I(x_2)G^0(x_2,x_1)h_I(x_1)G^0(x_1,x)$$
$$+(\frac{1}{\hbar})^3\int d^4x_1 d^4x_2 d^4x_3 G^0(x',x_3)h_I(x_3)G^0(x_3,x_2)h_I(x_2)$$
$$\times\; G^0(x_2,x_1)h_I(x_1)G^0(x_1,x) + \ldots\ldots , \qquad (3.15)$$

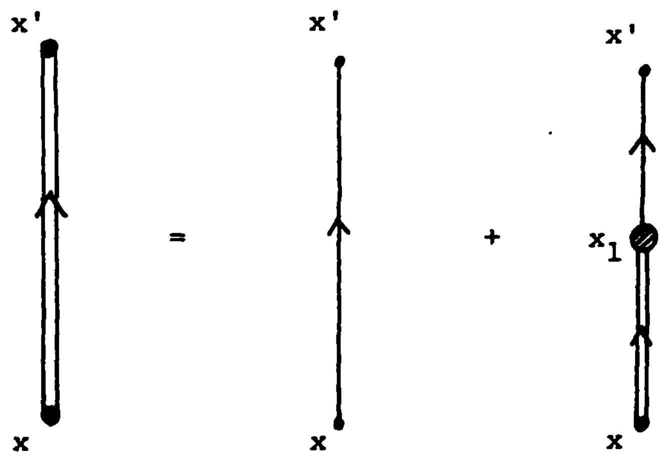
where G^0 is the "non-interacting" Green's function; and it leads to the Dyson's equation

$$G(x',x) = G^0(x',x) + \int d^4x_1 G^0(x',x_1)\Sigma(x_1)G(x_1,x) \qquad (3.16)$$

where $\Sigma(x)$, the proper self-energy, is simply given as

$$\Sigma(x) = \frac{h_I(x)}{\hbar} . \qquad (3.17)$$

Equation (3.16) can also be represented in the diagrammatic form



(3.18)

where the shaded circle stands for the proper self-energy.

We are now in a position to calculate $\tilde{G}(\vec{k}',\vec{k};\omega,t)$, the restricted Fourier Transform of $G(\vec{x}',t';x,t)$, by converting Eq.(3.16) into an algebraic equation. First we note that the QSA allows us to replace $\Sigma(\vec{x}_1,t_1)$ in Eq.(3.16) by $\Sigma(\vec{x}_1,t)$ [cf. discussion following Eq.(2.28)]. Dyson's equation can then be written

$$G(\vec{x}',t';\vec{x},t) = G^0(\vec{x}',t';\vec{x},t) + \int d^3x_1\int dt_1 G^0(\vec{x}',t';\vec{x}_1,t_1)\Sigma(\vec{x}_1,t) \times G(\vec{x}_1,t_1;\vec{x},t). \tag{3.19}$$

Fourier transforming with respect to t'-t, Eq.(3.19) becomes

$$\frac{1}{2\pi}\int d\omega e^{-i\omega(t'-t)}[G(x',x,\omega,t) - G^0(x',x,\omega)]$$
$$= \frac{1}{(2\pi)^2}\int d^3x_1\int dt_1\Sigma(\vec{x}_1,t)\int d\omega e^{-i\omega(t'-t_1)}G^0(\vec{x}',\vec{x}_1,\omega)\int d\omega' e^{-i\omega'(t_1-t)} \times G(\vec{x}_1,\vec{x},\omega',t), \tag{3.20}$$

since G^0 only depends on the difference of the time variables, $h_0(\vec{x})$ being time-independent. By first performing the integration with respect to t_1 and then ω', the right side of Eq.(3.20) can be expressed as

$$\frac{1}{(2\pi)^2}\int d\omega e^{-i\omega t'}\int d^3x_1 G^0(\vec{x}',\vec{x}_1,\omega)\Sigma(\vec{x}_1,t)\int d\omega' e^{i\omega' t}G(\vec{x}_1,\vec{x},\omega',t) \times \int dt_1 e^{i(\omega-\omega')t_1}$$
$$= \frac{1}{2\pi}\int d\omega e^{-i\omega t'}\int d^3x_1 G^0(\vec{x}',\vec{x}_1,\omega)\Sigma(\vec{x}_1,t)e^{i\omega t}G(\vec{x}_1,\vec{x},\omega,t)$$
$$= \frac{1}{2\pi}\int d\omega e^{-i\omega(t-t')}\int d^3x_1 G^0(\vec{x}',\vec{x}_1,\omega)\Sigma(\vec{x}_1,t)G(\vec{x}_1,\vec{x},\omega,t). \tag{3.21}$$

Eq.(3.20) then leads to the following Dyson's equation for $G(\vec{x}',\vec{x},\omega,t)$:

$$G(\vec{x}',\vec{x},\omega,t) = G^0(\vec{x}',\vec{x},\omega) + \int d^3x_1 G^0(\vec{x}',\vec{x}_1,\omega)\Sigma(\vec{x}_1,t)G(\vec{x}_1,\vec{x},\omega,t). \quad (3.22)$$

Next, the spatial Fourier transforms of $G(\vec{x}',\vec{x},\omega,t)$ are performed to obtain $\tilde{G}(\vec{k}',\vec{k},\omega,t)$. Eq.(3.22) can be written as

$$\frac{1}{(2\pi)^6} d^3k' d^3k e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}\cdot\vec{x}}[\tilde{G}(\vec{k}',\vec{k},\omega,t) - \tilde{G}^0(\vec{k}',\vec{k},\omega)]$$

$$= \frac{1}{(2\pi)^{12}}\int d^3x_1\, d^3k' d^3k_1 e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1} Z(\vec{k}',\vec{k}_1,\omega,t)\int d^3k_2 d^3k e^{i\vec{k}_2\cdot\vec{x}_1}$$

$$\times\, e^{i\vec{k}\cdot\vec{x}}\tilde{G}(\vec{k}_2,\vec{k},\omega,t), \quad (3.23)$$

where $Z(\vec{k}',\vec{k}_1,\omega,t) \equiv \int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{-i\vec{k}_1\cdot\vec{x}_1} G^0(\vec{x}',\vec{x}_1,\omega)\Sigma(\vec{x}_1,t)$. (3.24)

Again, by doing the appropriate integrations, we can reduce the right side of Eq.(3.23) as follows:

$$\frac{1}{(2\pi)^{12}}\int d^3k' d^3k e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}\cdot\vec{x}}\int d^3k_1 Z(\vec{k},\vec{k}_1,\omega,t)\int d^3k_2 \tilde{G}(\vec{k}_2,\vec{k},\omega,t)$$

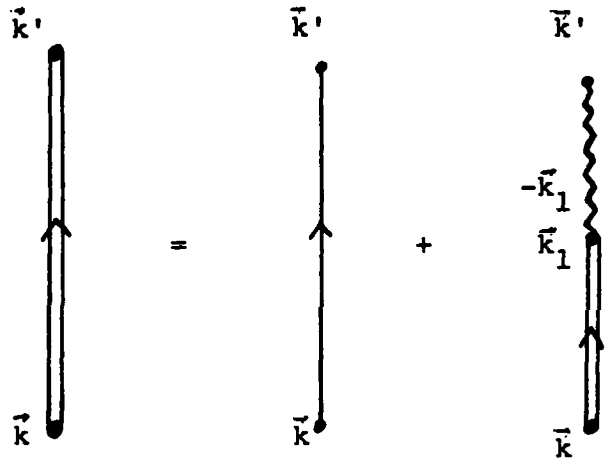
$$\times \int d^3x_1 e^{i(\vec{k}_1+\vec{k}_2)\cdot x_1} = \frac{1}{(2\pi)^9}\int d^3k' d^3k e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}\cdot\vec{x}}$$

$$\times \int d^3k_1 Z(\vec{k}',\vec{k}_1,\omega,t)\tilde{G}(-\vec{k}_1,\vec{k},\omega,t). \quad (3.25)$$

Comparison with Eq.(3.23) yields the Dyson's equation for $\tilde{G}(\vec{k}',\vec{k},\omega,t)$:

$$\tilde{G}(\vec{k}',\vec{k},\omega,t) = \tilde{G}^0(\vec{k}',\vec{k},\omega) + \frac{1}{(2\pi)^3}\int d^3k_1 Z(\vec{k}',-\vec{k}_1,\omega,t)\tilde{G}(\vec{k}_1,\vec{k},\omega,t), \quad (3.26)$$

which can also be written in the diagrammatic form



(3.27)

where the angular bar stands for the interaction $Z/(2\pi)^3$ and the intermediate momentum variables are to be integrated over.

At this point it is convenient to expand $\tilde{G}$ and $\tilde{G}^0$ as

$$\tilde{G}(\vec{k}',\vec{k},\omega,t) = \sum_{\alpha\beta} \tilde{\phi}^*_\alpha(-k')\tilde{\phi}_\beta(\vec{k})\tilde{G}_{\alpha\beta}(\omega,t), \tag{3.28}$$

$$\tilde{G}^0(\vec{k}',\vec{k},\omega) = \sum_{\alpha\beta} \tilde{\phi}_\alpha(-\vec{k}')\phi_\beta(\vec{k})\tilde{G}^0_\alpha(\omega)\delta_{\alpha\beta} \tag{3.29}$$

where each of the sums runs over the complete set of indices $\{i\}$ and $\{\sigma\}$ [i.e., the non-interacting adatom and surface states, cf. Eq. (3.4)] and

$$\tilde{\phi}_\alpha(\vec{k}) = \int d^3x e^{-i\vec{k}\cdot\vec{x}}\phi_\alpha(\vec{x}). \tag{3.30}$$

Expressing $G^0(\vec{x}',\vec{x}_1,\omega)$ also as

$$G^0(\vec{x}',\vec{x}_1,\omega) = \sum_\alpha \phi^*_\alpha(\vec{x}')\phi_\alpha(\vec{x}_1)\tilde{G}^0_\alpha(\omega), \tag{3.31}$$

we obtain the following form for $Z(\vec{k}',\vec{k},\omega,t)$:

$$Z(\vec{k}',\vec{k}_1,\omega,t) = \frac{1}{\hbar}\sum_{\alpha}\int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{-i\vec{k}_1\cdot\vec{x}_1}\phi^*_\alpha(\vec{x}')\phi_\alpha(\vec{x}_1)$$

$$\times\ h_I(\vec{x}_1,t)\tilde{G}^0_\alpha(\omega) = \sum_\alpha \tilde{\phi}^*_\alpha(-\vec{k}')\chi_\alpha(\vec{k}_1,t)\tilde{G}^0_\alpha(\omega), \qquad (3.32)$$

where

$$\chi_\alpha(\vec{k},t) \equiv \frac{1}{\hbar}\int d^3x_1 e^{-i\vec{k}_1\cdot\vec{x}_1}\phi_\alpha(\vec{x}_1)h_I(\vec{x}_1,t). \qquad (3.33)$$

Using Eqs.(3.28, (3.29), (3.32) and (3.33), Eq.(3.26) becomes

$$\sum_{\alpha,\beta}\tilde{\phi}_\alpha(-\vec{k}')\tilde{\phi}_\beta(\vec{k})[\tilde{G}_{\alpha\beta}(\omega,t) - \tilde{G}^0_\alpha(\omega)\delta_{\alpha\beta}]$$

$$= \frac{1}{(2\pi)^3}\int d^3k_1 \sum_\alpha \tilde{\phi}^*_\alpha(-\vec{k}')\chi_\alpha(-\vec{k}_1,t)G^0_\alpha(\omega)\sum_{\alpha'\beta}\tilde{\phi}^*_{\alpha'}(-\vec{k}_1)\tilde{\phi}_\beta(\vec{k})\tilde{G}_{\alpha'\beta}(\omega,t)$$

$$= \frac{1}{(2\pi)^3}\sum_{\alpha\beta}\tilde{\phi}^*_\alpha(-\vec{k}')\tilde{\phi}_\beta(\vec{k})\tilde{G}^0_\alpha(\omega)\sum_{\alpha'}\int d^3x_1\phi_\alpha(\vec{x}_1)\frac{h_I}{\hbar}(\vec{x}_1,t)\int d^3k_1 e^{i\vec{k}_1\cdot\vec{x}_1}$$

$$\times\ \tilde{\phi}^*_{\alpha'}(-\vec{k}_1)\tilde{G}_{\alpha'\beta}(\omega,t)$$

$$= \sum_{\alpha\beta}\tilde{\phi}_\alpha(-\vec{k}')\tilde{\phi}_\beta(\vec{k})\tilde{G}^0_\alpha(\omega)\sum_{\alpha'}\int d^3x_1\phi^*_{\alpha'}(\vec{x}_1)\frac{h_I}{\hbar}(\vec{x}_1,t)\phi_\alpha(\vec{x}_1)\tilde{G}_{\alpha'\beta}(\omega,t)$$

$$= \sum_{\alpha\beta}\tilde{\phi}^*_\alpha(-\vec{k}')\tilde{\phi}_\beta(\vec{k})\tilde{G}^0_\alpha(\omega)\sum_{\alpha'}\gamma^*_{\alpha\alpha'}(t)\tilde{G}_{\alpha'\beta}(\omega,t), \qquad (3.34)$$

where

$$\gamma_{\alpha'\alpha}(t) \equiv \int d^3x_1\phi^*_{\alpha'}(\vec{x}_1)\frac{h_I}{\hbar}(\vec{x}_1,t)\phi_\alpha(\vec{x}_1) \qquad (3.35)$$

may be considered to be a generalized time-dependent Rabi frequency. Eq.(3.34) yields immediately the algebraic Dyson's equation for $\tilde{G}_{\alpha\beta}(\omega,t)$:

$$\tilde{G}_{\alpha\beta}(\omega,t) - \tilde{G}^0_\alpha(\omega)\delta_{\alpha\beta} = \tilde{G}^0_\alpha(\omega)\sum_{\alpha'}\gamma^*_{\alpha\alpha'}\tilde{G}_{\alpha'\beta}(\omega,t) \qquad (3.36)$$

$$\text{or} \quad \sum_{\alpha'} \{ \frac{\delta_{\alpha'\alpha}}{\tilde{G}^0_\alpha(\omega)} - \gamma^*_{\alpha\alpha'}(t) \} \, \tilde{G}_{\alpha'\beta}(\omega,t) = \delta_{\alpha\beta} \, . \tag{3.37}$$

In matrix notation,

$$\underset{\approx}{G}(\omega,t) = \underset{\approx}{\Gamma}^{-1}(\omega,t), \tag{3.38}$$

where

$$\Gamma_{\alpha\beta} \equiv \frac{\delta_{\alpha\beta}}{\tilde{G}^0_\alpha(\omega)} - \gamma^*_{\alpha\beta}(t). \tag{3.39}$$

Since

$$\tilde{G}^0_\alpha(\omega) = \frac{1}{\omega-\omega_\alpha} \, , \tag{3.40}$$

where

$$\omega_\alpha \equiv \epsilon_\alpha/\hbar, \tag{3.41}$$

$$\Gamma_{\alpha\beta} = (\omega-\omega_\alpha)\delta_{\alpha\beta} - \gamma^*_{\alpha\beta}(t). \tag{3.42}$$

If we let

$$\vec{\mu}_{\alpha\beta} = e\langle\phi_\alpha|\vec{x}|\phi_\beta\rangle \, , \tag{3.43}$$

we have

$$\gamma_{ij}(t) = -\frac{1}{\hbar}\vec{E}_0\cdot\vec{\mu}_{ij}\theta(t) \cos\omega_L t \tag{3.44}$$

$$\gamma_{i\sigma}(t) = \frac{1}{\hbar}\{v_{i\sigma} - \vec{E}_0\cdot\vec{\mu}_{i\sigma}\theta(t)\cos\omega_L t\}, \tag{3.45}$$

and

$$\gamma_{\sigma\sigma'}(t) = -\frac{1}{\hbar}\vec{E}_0\cdot\vec{\mu}_{\sigma\sigma'}\theta(t) \cos\omega_L t. \tag{3.46}$$

Eqs.(3.28) and (3.38) then determine the time-dependent Green's function $\tilde{G}(\vec{k}',\vec{k},\omega,t)$.

$\tilde{G}$ is related to $\tilde{G}_A$, the advanced Green's function, through the following relationships:

$$\begin{aligned} \tilde{G}_A(\vec{p},\omega,t) &= \tilde{G}(\vec{p},\vec{p},\omega,t), \qquad \omega < \mu(t)/\hbar \\ &= \tilde{G}^*(\vec{p},\vec{p},\omega,t), \qquad \omega > \mu(t)/\hbar \end{aligned} \tag{3.47}$$

where $\mu(t)$ is the time-dependent chemical potential of the adatom-surface-field system. According to the Lehmann representation,[22] $\mu(t)$ is determined as the point in real ω space at which the imaginary parts of the poles of $\tilde{G}$ (regarded as a function of ω) change sign. These poles are determined by Eqs.(3.38) and (3.42). Eq.(2.26) can then be used to give the spectral function.

IV. Conclusion

We have proposed a non-perturbative formalism to treat the bound-continuum (BC) problem of collisional ionization of solid surfaces. This formalism has certain advantages over conventional treatments of BC problems. First it provides a direct way of obtaining differential cross sections with respect to the continuum of emitted electronic energies, whereas the usual optical potential methods would only lead to the total cross section. Second, it bypasses the approximation of limiting the problem to a finite number of channels, usually two, that is often required in coupled-channels approaches. Further, it renders the discretization of electronic energies unnecessary, which is again the standard procedure in coupled-channels as well as semiclassical treatments.

The QSA and the IMA, however, pose limitations on the validity and usefulness of the present approach. In situations where the applied field has frequencies ω_L large compared to or of the order of $1/\tau$, the QSA breaks down, although the IMA may still be applicable to the field-free problem. Fields with large ω_L may by themselves lead to electronic excitation or ionization, and the inclusion of collisional effects may not necessarily provide extra information

on the systems of interest. However, the general collisional problem with arbitrarily variable ω_L is definitely of immense theoretical interest. It should also be noted that the underlying criterion for the validity of both the QSA and the IMA is the shortness of the collision time τ. With the relaxation of this criterion to the extent that the IMA is no longer valid, electron correlation effects will have to be considered which would render the Green's function formalism much more complicated than the present treatment.

Appendix I

In this appendix we will derive the Dyson's equation for the quantity $\tilde{G}(\vec{p}_1,\omega,t)$ [cf. Eq.(2.29)]. We start from Eq.(3.16):

$$G(\vec{x}',t';\vec{x},t) = G^0(\vec{x}',t';\vec{x},t) + \int d^3x_1 \int dt_1 G^0(\vec{x}',t';\vec{x}_1,t_1) \times \Sigma(\vec{x}_1,t_1)G(\vec{x}_1,t_1;\vec{x},t). \tag{A.1}$$

It should be noted this equation differs from Eq.(3.19) [which is used to obtain the restricted Fourier Transform $\tilde{G}(\vec{p}_1,\omega,t)$] only in the time variable in the proper self-energy Σ. Fourier Transforming with respect to t'-t, Eq.(A.1) becomes

$$\frac{1}{2\pi}\int d\omega e^{-i\omega(t'-t)}[G(\vec{x}',\vec{x},\omega,t) - G^0(\vec{x}',\vec{x},\omega)]$$
$$= \frac{1}{(2\pi)^2}\int d^3x_1 \int dt_1 \Sigma(\vec{x}_1,t_1)\int d\omega e^{-i\omega(t'-t_1)} G^0(\vec{x}',\vec{x}_1,\omega)\int d\omega' e^{-i\omega'(t_1-t)} \times G(\vec{x}_1,\vec{x},\omega',t). \tag{A.2}$$

From Eqs.(3.17) and (3.10)

$$\Sigma(\vec{x}_1,t_1) = \frac{1}{\hbar}\{h_1(\vec{x}_1) - e\vec{E}_0\cdot\vec{x}_1\theta(t_1)\cos\omega_L t_1\}.$$

The t_1-integration on the right side of Eq.(A.2) can then be written as:

$$\int dt_1 \Sigma(\vec{x}_1,t_1)e^{-i(\omega'-\omega)t_1}$$
$$= \frac{2\pi}{\hbar}h_1(\vec{x}_1)\delta(\omega'-\omega) - \frac{1}{\hbar}e\vec{E}_0\cdot\vec{x}_1\int_{-\infty}^{\infty}dt_1\, e^{-i(\omega'-\omega)t_1}\theta(t_1)\cos\omega_L t_1$$
$$= \frac{2\pi}{\hbar}h_1(\vec{x}_1)\delta(\omega'-\omega) - \frac{i}{2\hbar}e\vec{E}_0\cdot\vec{x}_1\{\frac{1}{\omega+\omega_L-\omega'+i\eta} + \frac{1}{\omega-\omega_L-\omega'+i\eta}\}, \tag{A.3}$$

where η is a vanishingly small positive quantity, and the integral representation for $\theta(t)$ [Eq.(2.23)] has been used. Performing the ω' integration next, we find that

$$G(\vec{x}',\vec{x},\omega,t) - G^0(\vec{x}',\vec{x},\omega)$$

$$= \int d^3x_1 G_0(\vec{x}',\vec{x}_1,\omega)[\frac{h_1(\vec{x}_1)}{\hbar} G(\vec{x}_1,\vec{x},\omega,t) - \frac{e\vec{E}_0\cdot\vec{x}_1}{2\hbar}$$

$$\times \{e^{i\omega_L t}\int\frac{d\omega''}{2\pi i}\,\frac{e^{i\omega'' t}}{\omega''-i\eta}\,G(\vec{x}_1,\vec{x},\omega''+\omega+\omega_L,t)$$

$$+ e^{-i\omega_L t}\int\frac{d\omega''}{2\pi i}\,\frac{e^{i\omega'' t}}{\omega''-i\eta}\,G(\vec{x}_1,\vec{x},\omega''+\omega-\omega_L,t)\}]. \qquad (A.4)$$

The spatial Fourier Transforms are then performed by rewriting Eq.(A.4) as follows:

$$\frac{1}{(2\pi)^6}\int d^3k' d^3k e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}\cdot\vec{x}}[\tilde{G}(\vec{k}',\vec{k},\omega,t) - \tilde{G}^0(k',k,\omega)]$$

$$= \frac{1}{(2\pi)^{12}}\int d^3x_1\int d^3k' d^3k_1 e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1} Z_1(k',k_1,\omega)\int d^3k_2 d^3k e^{i\vec{k}_2\cdot\vec{x}_1} e^{i\vec{k}\cdot\vec{x}}$$

$$\times \tilde{G}(\vec{k}_2,\vec{k},\omega,t) + \frac{1}{(2\pi)^{12}}\,\frac{e^{i\omega_L t}}{2}\int d^3x_1\int d^3k' d^3k_1 e^{i\vec{k}\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1}$$

$$Z_2(\vec{k}',\vec{k}_1,\omega)\int\frac{d\omega''}{2\pi i}\,\frac{e^{i\omega'' t}}{\omega''-i\eta}\int d^3k_2 d^3k e^{i\vec{k}_2\cdot\vec{x}_1} e^{i\vec{k}\cdot\vec{x}}\tilde{G}(\vec{k}_2,\vec{k},\omega''+\omega-\omega_L,t)$$

$$+ \frac{1}{(2\pi)^{12}}\,\frac{e^{-i\omega_L t}}{2}\int d^3x_1\int d^3k' d^3k_1 e^{i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1} Z_2(\vec{k}',\vec{k}_1,\omega)\int\frac{d\omega''}{2\pi i}$$

$$\times \frac{e^{i\omega'' t}}{\omega''-i\eta}\int d^3k_2 d^3k e^{i\vec{k}_2\cdot\vec{x}_1} e^{i\vec{k}\cdot\vec{x}}\tilde{G}(\vec{k}_2,\vec{k},\omega''+\omega-\omega_L,t) \qquad (A.5)$$

where

$$Z_1(\vec{k}',\vec{k}_1,\omega) = \int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{-i\vec{k}_1\cdot\vec{x}_1}\,\frac{h_1}{\hbar}(\vec{x}_1) G^0(\vec{x}',\vec{x}_1,\omega), \qquad (A.6)$$

and

$$Z_2(\vec{k}',\vec{k}_1,\omega) = \int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{-i\vec{k}_1\cdot\vec{x}_1} \left(-\frac{e\vec{E}_0\cdot\vec{x}_1}{\hbar}\right) G^0(\vec{x}',\vec{x}_1,\omega) . \quad \text{(A.7)}$$

By first performing the x_1 and then the $\vec{k}_2$ integration, we obtain the Dyson's equation for $\tilde{G}(\vec{k}',\vec{k},\omega,t)$:

$$\tilde{G}(\vec{k}',\vec{k},\omega,t) - \tilde{G}^0(\vec{k}',\vec{k},\omega) = \frac{1}{(2\pi)^3}\int d^3k_1 Z_1(\vec{k}',-\vec{k}_1,\omega)\tilde{G}(\vec{k}_1\vec{k},\omega,t)$$

$$+ \frac{1}{(2\pi)^3}\int d^3k_1 Z_2(\vec{k}',-\vec{k}_1,\omega) \left[\frac{e^{i\omega_L t}}{2}\int\frac{d\omega''}{2\pi i}\frac{e^{i\omega'' t}}{\omega''-i\eta}\tilde{G}(\vec{k}_1,\vec{k},\omega''+\omega+\omega_L,t)\right.$$

$$\left. + \frac{e^{-i\omega_L t}}{2}\int\frac{d\omega''}{2\pi i}\frac{e^{i\omega'' t}}{\omega''-i\eta}\tilde{G}(\vec{k}_1,\vec{k},\omega''+\omega-\omega_L,t)\right] . \quad \text{(A.8)}$$

We again invoke the expansions [cf. Eqs.(3.28), (3.29) and (3.31)]:

$$G^0(\vec{x}',\vec{x}_1,\omega) = \sum_\alpha \phi_\alpha^*(\vec{x}')\phi_\alpha(\vec{x}_1)\tilde{G}_\alpha^0(\omega) , \quad \text{(A.9)}$$

$$\tilde{G}^0(\vec{k}',\vec{k},\omega) = \sum_{\alpha\beta} \tilde{\phi}_\alpha^*(-\vec{k}')\tilde{\phi}_\beta(\vec{k})\tilde{G}_\alpha^0(\omega)\delta_{\alpha\beta} , \quad \text{(A.10)}$$

and

$$\tilde{G}(\vec{k}',\vec{k},\omega,t) = \sum_{\alpha\beta} \tilde{\phi}_\alpha^*(-\vec{k}')\phi_\beta(\vec{k})\tilde{G}_{\alpha\beta}(\omega,t) . \quad \text{(A.11)}$$

The interaction terms Z_1 and Z_2 can then be written:

$$Z_1(\vec{k}',-\vec{k}_1,\omega) = \sum_\alpha\int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1}\phi_\alpha^*(\vec{x}')\phi_\alpha(\vec{x}_1)\frac{h_1(\vec{x}_1)}{\hbar}\tilde{G}_\alpha^0(\omega)$$

$$= \sum_\alpha \tilde{\phi}_\alpha^*(-\vec{k}')\chi_\alpha^{(1)}(-\vec{k}_1)\tilde{G}_\alpha^0(\omega) , \quad \text{(A.12)}$$

$$Z_2(\vec{k}',-\vec{k}_1,\omega) = \sum_\alpha\int d^3x' d^3x_1 e^{-i\vec{k}'\cdot\vec{x}'} e^{i\vec{k}_1\cdot\vec{x}_1}\phi_\alpha^*(\vec{x}')\phi_\alpha(\vec{x}_1)\left(\frac{-e\vec{E}_0\cdot\vec{x}_1}{2\hbar}\right)\tilde{G}_\alpha^0(\omega)$$

$$= \sum_\alpha \tilde{\phi}_\alpha^*(-\vec{k}')\chi_\alpha^{(2)}(-\vec{k}_1)\tilde{G}_\alpha^0(\omega) , \quad \text{(A.13)}$$

where

$$\chi_\alpha^{(1)}(\vec{k}_1) \equiv \int d^3x_1 e^{-i\vec{k}_1\cdot\vec{x}_1}\phi_\alpha(\vec{x}_1)\frac{h_1(\vec{x}_1)}{\hbar}, \tag{A.14}$$

and

$$\chi_\alpha^{(2)}(\vec{k}_1) \equiv \int d^3x_1 e^{-i\vec{k}_1\cdot\vec{x}_1}\phi_\alpha(\vec{x}_1)\left(\frac{-e\vec{E}_0\cdot\vec{x}_1}{\hbar}\right). \tag{A.15}$$

Finally, we perform the $\vec{k}_1$ integration on the right hand side of Eq.(A.8) and thus obtain [following the procedure in Eq.(3.34)] the Dyson's equation for $\tilde{G}_{\alpha\beta}(\omega,t)$:

$$\tilde{G}_{\alpha\beta}(\omega,t) = \tilde{G}_\alpha^0(\omega)[\delta_{\alpha\beta} + \sum_{\alpha'}\gamma_{\alpha\alpha'}^{(1)*}\tilde{G}_{\alpha'\beta}(\omega,t)$$

$$+ \sum_{\alpha'}\gamma_{\alpha\alpha'}^{(2)*}\{\frac{e^{i\omega_L t}}{2}\int\frac{d\omega''}{2\pi i}\frac{e^{i\omega'' t}}{\omega''-i\eta}\tilde{G}_{\alpha'\beta}(\omega''+\omega+\omega_L,t) + \frac{e^{-i\omega_L t}}{2}\int\frac{d\omega''}{2\pi i}\frac{e^{i\omega'' t}}{\omega''-i\eta}$$

$$\times\ \tilde{G}_{\alpha'\beta}(\omega''+\omega-\omega_L,t)\}] \tag{A.16}$$

where

$$\gamma_{\alpha'\alpha}^{(1)} \equiv \int d^3x\phi_{\alpha'}^*(\vec{x})\frac{h_1(\vec{x})}{\hbar}\phi_\alpha(\vec{x}), \tag{A.17}$$

$$\gamma_{\alpha'\alpha}^{(2)} \equiv \int d^3x\phi_{\alpha'}^*(\vec{x})\left(\frac{-e\vec{E}_0\cdot\vec{x}}{\hbar}\right)\phi_\alpha(\vec{x}), \tag{A.18}$$

which may again be considered as Rabi frequencies [cf. Eq.(3.35)]. In matrix notation Eq.(A.16) can be written as

$$\underset{\approx}{I} = \underset{\approx}{\Gamma}^{(1)}\cdot\underset{\approx}{G}(\omega,t) - \frac{1}{2}\underset{\approx}{\gamma}^{(2)*}\cdot\{e^{i\omega_L t}\int\frac{d\omega'}{2\pi i}\frac{e^{i\omega' t}}{\omega'-i\eta}\underset{\approx}{G}(\omega'+\omega+\omega_L,t) + e^{-i\omega_L t}$$

$$\times\ \int\frac{d\omega'}{2\pi i}\frac{e^{i\omega' t}}{\omega'-i\eta}\underset{\approx}{G}(\omega'+\omega-\omega_L,t)\} \tag{A.19}$$

where

$$\Gamma_{\alpha\beta}^{(1)} \equiv \frac{\delta_{\alpha\beta}}{\tilde{G}_\alpha^0(\omega)} - \gamma_{\alpha\beta}^{(1)*}. \tag{A.20}$$

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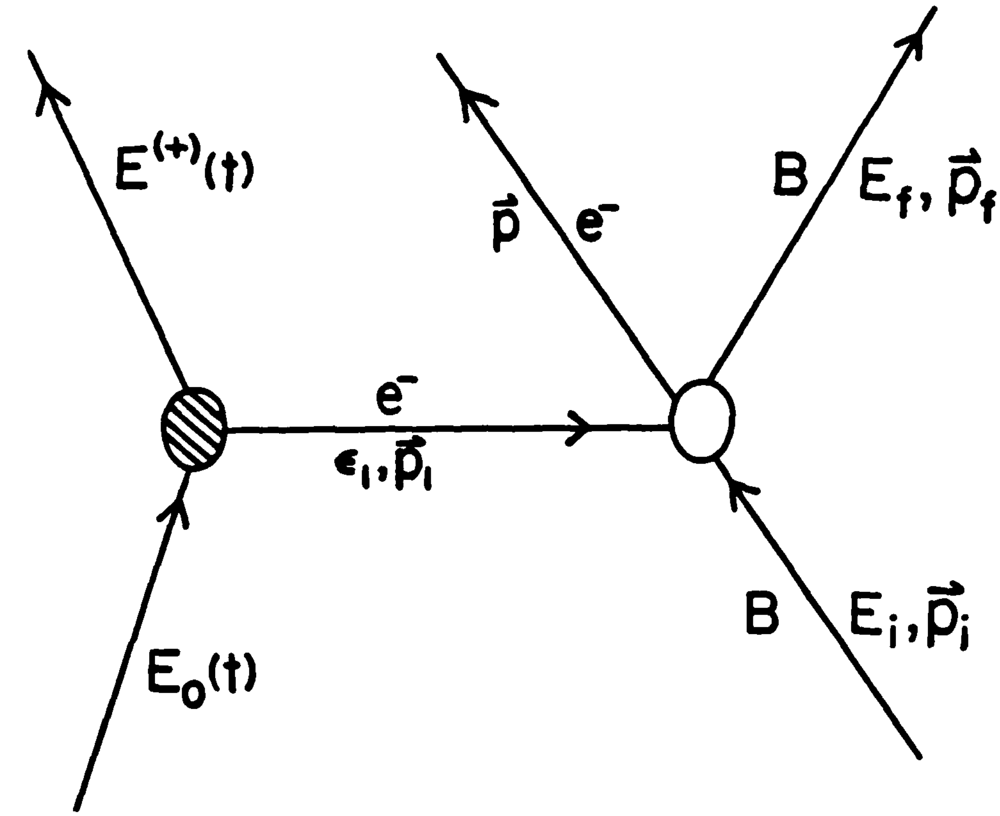
Figure 1. Schematic representation of the transition matrix element T(t). The shaded circle represents the hole momentum distribution function $\langle\Psi_0^{(+)}(t)|\hat{a}(\vec{p}_1)|\Psi_0(t)\rangle$ for the adatom-surface + field system whereas the blank circle represents the electron-atom scattering matric element $T_{E_f,\vec{p}_f,\vec{p};E_i,\vec{p}_i,\vec{p}_1}$. At the shaded circle, energy is adiabatically conserved; and at the blank circle, energy and momentum are strictly conserved.



$E^{(+)}(t)$
$\vec{p}$
e^-
B
$E_f, \vec{p}_f$
e^-
$\epsilon_1, \vec{p}_1$
B
$E_i, \vec{p}_i$
$E_0(t)$

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